Computer Simulation of Liquid Crystal Polymer Systems with Complex Topology

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Academic Dissertation

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PREFACE

This work has been carried out in the Laboratory of Polymer Chemistry, University of Helsinki. The work has been carried out during 2000-2004 under the supervision of Professor Franciska Sundholm and Professor Anatoly Darinskii.

I wish to express my deepest gratitude to my supervisors Professor Franciska Sundholm and Professor Anatoly Darinskii for guidance, encouraging, patience, criticism and fruitful discussions, and for providing the facilities necessary for the studies. I also wish to thank Dr. Igor M. Neelov for the numerous discussions that have had a fundamental effect on the work and Dr. Nikolaj K. Balabaev for assistance in computer codes. Their contribution as co-authors of the presented publications is gratefully acknowledged.

I also wish to thank Professor Heikki Tenhu, the head of the Laboratory of Polymer Chemistry, for providing facilities and creating an inspiring and free work environment. I appreciate the friendly assistance of the former and current personnel of the Laboratory of Polymer Chemistry.

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ABSTRACT

The static and dynamic characteristics of liquid crystal (LC) systems with complex topology have been studied by the method of molecular dynamics. Three systems were simulated. The first is the system of short semi-flexible linear molecules (mesogens) with non-uniform distribution of flexibility along the chain. The second system is a flexible polymer network swollen in the solvent consisting of mesogens with uniform flexibility. The third one – a polymer network consisting of crosslinked polymer chains with mesogenic side groups. As a mesogen model short chains comprising several beads with repulsive intermolecular interactions were used. All considered systems are able to form a lyotropic LC phase under the increase of the density due to the anisotropy of mesogens. Phase behaviour, internal structure and mobility were studied. For the first model only the nematic phase was obtained in contrast to the systems with uniform flexibility of mesogens where both nematic and smectic phases were observed. The second model was assumed to describe a polymer dispersed liquid crystals. Increasing of the density in the composite system the LC solvent experiences the same phase transitions as the pure one. The presence of the network shifts the isotropic - nematic transition to higher densities but does not change the position of the nematic - smectic transition. The third system was assumed to describe LC elastomers. It was obtained from the second system through attachment of mesogen ends to the polymer network. The position of the isotropic - nematic transition does not change significantly but the region of the existence of the smectic phase shifts to lower densities.

For all the systems the anisotropy of translational mobility of mesogenic groups was observed. In particular it was shown that in the nematic phase the anisotropy of translational diffusion and ratio of translational and rotational diffusion coefficients depends only on the order parameter. The LC ordering leads also to some anisotropy of mobility of chain monomers. The sign of this anisotropy corresponds to that for mesogens.

LIST OF ABBREVIATIONS AND SYMBOLS

LC Liquid crystal

MD Molecular dynamics

MC Monte Carlo

NPT Constant temperature and pressure ensemble

NVT Constant temperature and volume ensemble

LJ Lennard-Jones potential

FENE Finitely extendible nonlinear elastic potential

MSD Mean square displacement

PDLC Polymer dispersed liquid crystals

α elastic constant

$\beta_{p,\alpha}$ parameter of Berendsen barostat

σ, ε Lennard-Jones parameters

ρ number density

$\delta(t)$ Dirac's delta function

θ angle between the end-to-end vector of the molecule and the director

λ collision frequency

τ reduced time unit

d diameter of the mesogen

D, D_{par}, D_{per} translational self-diffusion coefficient and its projections

D_{rot} rotational diffusion coefficient

$f^{i}_{k,\alpha}$ components of momentum

$g(h)$ distribution function of the end-to –end distance

$g(z)$ binary distribution function along the axis of regularity

$\langle h^2 \rangle$ mean square end-to-end distance

K_s spring elasticity constant

l bond length

l_p persistence length

$n_{\alpha,\beta}$ components of the normalized end-to-end vector of the molecule

N_c numbers of particles in the mesogen

N_m number of mesogens in the system

p aspect ratio

$P_1(t)$, $P_2(t)$ correlation functions

P_α components of the instantaneous pressure tensor

P_{ref} prescribed pressure

$< \Delta r_{par}^2(t) >$ mean square displacements along the axis of regularity

$< \Delta r_{per}^2(t) >$ mean square displacements perpendicular the axis of regularity

S order parameter

$S_2(r)$ orientational pair correlation function

T_{ref} bath temperature

V volume of the simulation box

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following six publications, which are referred in the text by their Roman numerals I-VI:

I. N. Balabaev, A. Darinskii, I.Neelov, A.Zarembo, F.Sundholm. Computer simulation of liquid-crystal system consisting of semi-flexible rod-like linear molecules. Polym. Sci. A, 2002, **44**, 1146

II. A.A. Darinskii, I.M. Neelov, A. Zarembo, N.K. Balabaev, F. Sundholm, K. Binder. Computer simulation of the liquid crystal formation in a semi-flexible polymer system. Macromol. Symposia, 2003, **191,** 191

III. A. Darinskii, A. Zarembo, N. Balabaev, I.Neelov, F.Sundholm. Anisotropy of diffusion in a liquid crystalline system of semi-flexible polymer chains. Phys.Chem.Chem. Phys, 2003, **5**, 2410

IV. A. Darinskii, A.Zarembo, N. Balabaev, I.Neelov, F.Sundholm. Molecular dynamics simulation of a flexible polymer network in a liquid crystal solvent: structure and equilibrium properties. Polymer, 2004, **45**, 4857

V. A. Darinskii, N. A.Zarembo, Balabaev, I. Neelov, F.Sundholm. Molecular dynamics simulation of a flexible polymer network in a liquid crystal solvent: dynamical properties. Polymer, 2004, **45**, 8901

VI A.Zarembo, A.Darinskii, I.Neelov, N.Balabaev, F.Sundholm Molecular dynamics simulation of liquid crystalline networks and flexible polymer network in liquid crystal solution. In book “Slow Dynamics in Complex Systems”, AIP conference proceedings, 2004, **708**, 452

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AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

Publication I deals with the study of the model for flexible mesogen in a pure LC system. Here the other authors were primarily responsible for the idea of the model and methodology of implementation. The author of the thesis designed and conducted the practical part of the study. The article was written in close collaboration with Prof. Darinskii.

In Publication II the author was responsible for the first part of the article dealing with the low molecular liquid crystal.

The dynamical behaviour of a LC system of semiflexible molecules is described in Publication III. The original idea of using wobbling in the cone model was suggested by Prof. Darinskii. The author was responsible for implementation of this model and for all the simulations and data analyses and processing. The article was written in close collaboration with Prof. Darinskii.

Publications IV and V deal with simulation of a LC in polymer network and in a linear polymer. The research plan, selection of the model and methodology of the implementation of simulation was developed in close collaboration with Prof. Darinskii and Dr. Balabaev. The author carried out the practical part and wrote the publications.

The results concerning the polymerized LC system with side chain mesogens are presented in publication VI. The methods for simulation of the formation of the LC elastomer system were originated by Dr. Balabaev. The author drew up the research plan, carried out simulation and wrote the publication.

CONTENT

1. Introduction

Liquid crystals (LC) have many applications due to their unique combination of solid and liquid properties. The order in LC occurs due to two factors: shape anisotropy of molecules and temperature dependent anisotropic interactions between them. The thermotropic LC transitions are initiated by changes in temperature and observed in systems where the anisotropic interactions are strong enough. When the shape anisotropy is dominant the lyotropic liquid crystals are formed in solutions by the change in concentration. In the present work only lyotropic LC will be considered.

Three systems which are able to form LC state were studied. The first is the system of short semi-flexible linear molecules (mesogens) with non-uniform distribution of flexibility along the chain. The second is flexible polymer network swollen in the solvent consisting of mesogens with uniform flexibility. The third one – a polymer network consisting of crosslinked polymer chains with mesogenic side groups.

For the study of these systems the molecular dynamics method was used. The computer simulation has presently become a very powerful method in the molecular physics and allows to obtain in some cases information about the molecular structure and mobility which is non-accessible by usual experimental methods.

The reasons for the choice of these systems for the study were following ones. Low molecular LC systems have been rather extensively studied during the past 50 years both by analytical methods [1-3] and by computational methods [4-7]. A number of models are developed to describe the behaviour of rigid mesogens [8-10]. However, many real LC molecules have some flexibility [11]. The flexibility results in a varying phase behaviour [12] which is important for biology, electronics and materials science [13]. Usually the models with uniformly distributed flexibility along the mesogen were considered [4-7]. In the present work the model of the mesogen where flexibility is non uniformly distributed along the molecule will be considered. The phase behaviour of this system under the change of the concentration (density) as well as internal dynamics in different phase state will be studied and compared with corresponding results for semi-flexible models with uniform flexibility.

Polymer / LC composites have a great potential in many applications. One of most widely used types of such composites is a polymer-dispersed liquid crystal (PDLC). It is a promising material for reflective and projecting displays, window shutters, holographic recording media etc. [13]. The morphology of PDLC and its dependence

on the condition of the preparation have been widely studied [14-16]. There are also some theoretical studies of the phase behaviour of polymer-LC blends [17-19]. The effect of the polymer network on the phase behaviour and dynamics of low molecular LC has been studied much less. In the present work the system consisting of a polymer network swollen in a LC solvent is considered. The main issue is how the presence of the flexible network influences the low molecular LC solvent. To our knowledge there are no theoretical studies concerning such systems.

LC elastomers attracted the attention of researchers for a long time. They combine mechanical properties due to the entropic elasticity of chains with long range orientational order and mobility characteristic for low molecular LC. There are many experimental works devoted to the synthesis, structure and outstanding mechanical properties of LC elastomers [20]. There are also some theoretical studies [21] of these systems and works devoted to the simulation of main chain LC polymers with rigid mesogens [22, 23]. However, the dynamic behaviour of LC elastomers is still quite unclear [24]. Computer simulation of side chain LC elastomers are practically absent to our knowledge. In the present work the simple model of a polymer network with mesogenic side chain mesogens is considered. Its phase behaviour is simulated and compared with the system of a polymer network in low molecular LC solvent.

For all the systems both structural and dynamical properties were studied and compared with available experimental data and analytical theory predictions.

2. Simulation details

The simulation was performed by the molecular dynamics method. The motion of each particle in the system is described by Newtonian equations with additional terms for keeping constant pressure and temperature. The collisional thermostat [25, 26] was applied to get local thermal equilibrium and the Berendsen barostat [27] was used to maintain the prescribed pressure. The calculations for an NPT ensemble (constant temperature and pressure) [28] have been carried out according to the following modified Newtonian equations

$$\frac{dr_{i,\alpha}}{dt} = v_{i,\alpha} + \beta_{p,\alpha} \cdot \left(P_\alpha - P_{\alpha,ref}\right) \cdot r_{i,\alpha} \qquad (1)$$

$$m_i \frac{dv_{i,\alpha}}{dt} = F_{i,\alpha} + \sum_k f^i_{k,\alpha} \cdot \delta\left(t - t^i_k\right) \qquad (2)$$

where m_i, $r_{i,\alpha}$, $v_{i,\alpha}$, (α={x, y, z}) are masses, coordinates, velocities and forces for i-th particle ($i=1,..., N$). $F_{i,\alpha}$ is a α- component of the force affecting i-th particle, $\beta_{p,\alpha}$ - parameter of barostat; P_{ref} is the prescribed pressure; $P_\alpha \equiv P_{\alpha\alpha}$ are components of the instantaneous pressure tensor [27]:

$$P_{\alpha\alpha} = V^{-1}(2/3 E_{kin} + \sum_{ij,i<j} r_{ij,\alpha} F_{ij,\alpha})) \qquad (3)$$

where V is the volume of the simulation box, E_{kin} is the kinetic energy of the system. The additional term in the equation (2) is responsible for keeping the temperature. Here $f^i_{k,\alpha}$ are components of momentum acting on bead i in an accidental time moment t^i_k as a result of collision with a virtual bath particle; $\delta(t)$ is Dirac's delta function. A thermostat is implemented by stochastic collisions of each particle with virtual particles having velocity chosen from a Gaussian distribution.

Periodic boundary conditions in three directions x, y, z were used. The equations of motion were integrated using the «velocity Verlet» algorithm [28]. The integration step is t=0.004. The reduced unit for time $\tau = \sigma (m/\varepsilon)^{1/2}$ was used. All calculations were performed at the same reduced bath temperature T_{ref} equal to unity. The equilibrium state was considered being achieved after the characteristics of the system (density and order parameter) became stable on a sufficiently long part of the trajectory. The calculations were carried out using computer time provided by the Centre of Scientific Computing (CSC, Espoo, Finland) on IBM eServer Cluster 1600.

2.1. Calculated characteristics

2.1.1 Structure characteristics

2.1.1.2. Order parameter

The formation of the LC phase was followed from the behaviour of order parameter S which was determined as

$$S = \frac{3}{2}\left\langle \cos^2\theta - \frac{1}{3}\right\rangle, \qquad (4)$$

where θ is the angle between the end-to-end vector of the molecules and the director [29]. The director was calculated by the diagonalization of the ordering tensor

$$Q_{\alpha\beta} = \frac{1}{N_m}\sum_{j=1}^{N_m}\frac{3}{2}n_{j\alpha}n_{j\beta} - \frac{1}{2}\delta_{\alpha\beta}, \quad (5)$$

where $n_{j\alpha}$ are components of the normalized end-to-end vector of the molecule *j*; α, β =x, y, z; δ is the delta function [30]. The eigenvector corresponding to the maximum eigenvalue λ_1 shows the direction of the preferred orientation of the molecules. The value of λ_1 gives the value of *S*.

2.1.1.3. Chain conformation

The size of the chain and its conformation were characterized by mean square of the distances between their ends $<h^2>$ and radii of gyration $<Rg^2>$ and its projection on the axis of regularity and in the perpendicular direction. Also the distribution functions of the end-to-end distance *g(h)* and its projections on the axis of regularity and in perpendicular direction were calculated.

2.1.1.4. Binary distribution function along the axis of regularity

The binary distribution function *g(z)* of the centres of mass of mesogens along the axis of regularity is defined as

$$g(z) = \frac{V}{N_m^2}\left\langle \sum_i \sum_{j\neq i} \delta(z - z_{ij}) \right\rangle \quad (6)$$

where $z_{ij}=|z_i-z_j|$ is the distance between projections of the centres of mass of *i* and *j* mesogens on axis OZ; N_m is the number of mesogens in the system.

This function was used to distinguish between the smectic and nematic phases. For nematic and isotropic phases the distribution along the axis OZ is uniform. The layered structure of LC, which is typical for the smectic phase tend to the periodic character of the distribution function.

2.1.1.5. Density profiles of beads of chains along axis of regularity

The morphology of the systems can be characterised by density profiles of beads along axis OZ. The number density is calculated by

$$\rho_A(z) = \left\langle \sum_i \delta(z - z_{Ai}) \right\rangle \quad (7)$$

where z_i is a position of *i*-bead, A=*L, n*.

2.1.1.6. Orientational pair correlation function

This function allows the determination of the relative orientation of molecules as a function of distance [28]. The orientational pair correlation function $S_2(r)$ is defined as

$$S_2(r) =< P_2(\cos\theta_{ij}(r)) > \quad (8)$$

where $cos\Theta ij(r) = \mathbf{a}_i\mathbf{a}_j/|\mathbf{a}_i||\mathbf{a}_j,|$ and $\mathbf{a}_i$ and $\mathbf{a}_j$ are the vectors of the major axes of molecules i and j calculated by diagonalization the inertia tensor of the molecules.

2.1.2 Dynamic characteristics

2.1.2.1 Translational diffusion

To study the translational mobility the time dependences of the mean square displacements (MSD) of the centres of mass of mesogens and chain monomers along the axis of regularity $< \Delta r_{par}^2(t) >$ and in the perpendicular direction $< \Delta r_{per}^2(t) >$ were calculated. If the motion is purely diffusive the MSD vs. time is a linear dependence and the diffusion coefficients D_{par} and D_{per} can be calculated from the slopes of the corresponding curves using equations $< \Delta r_{par}^2(t) >= 2D_{par}t$ and $< \Delta r_{per}^2(t) >= 2D_{per}t$ [28]. «Isotropic» value of the self-diffusion coefficient is defined as in [31]

$$D = (2D_{per} + D_{par}) / 3 \quad (9)$$

The anisotropy of diffusion was estimated from the ratio D_{par} / D_{per}. The translational anisotropy is one of the most interesting dynamic features of the LC phase.

2.2.2.2. Rotational diffusion

For characterization of the orientational mobility of mesogens the orientation correlation functions

$$P_1 = \langle \cos\theta(t) \rangle \text{ and } P_2 = \frac{3}{2}(\langle \cos^2\theta(t) \rangle - 1/3) \quad (10)$$

were calculated. $\theta(t)$ is an angle of rotation of the long axis for the time t.

For the rigid particle in a viscous medium

$$P_2(t) = P_1^3(t) \quad (11)$$

and

$$P_2(t) = \exp(-6D_{rot}t) \quad (12)$$

where D_{rot} is the rotational diffusion coefficient.

For rigid cylinders in the homogeneous solvent the analytical expressions were obtained [32]:

$$D_{rot} = \frac{3D_o}{\pi L^2}(\ln p - 0.662 + 0.917/p - 0.050/p^2) \quad (13)$$

$$D = \frac{D_o}{3\pi}(\ln p + 0.312 + 0.565/p - 0.100/p^2) \quad (14)$$

with $D_0=k_BT/\eta L$, where η is the shear viscosity of the solvent, L is the length of the cylinder and p is the aspect ratio.

In the LC state the rotational mobility of mesogens is restricted and the correlation functions $P_1(t)$ and $P_2(t)$ do not decay to zero. For the analysis of rotational motions of molecules in the nematic state a wobbling in a cone model can be applied [32]. In this model the rotational diffusion of a particle assumed to be free within a cone of semiangle θ_o and forbidden on the outside. The value of θ_o can be estimated from the equation:

$$\cos\theta_o(1+\cos\theta_o) = 2S \quad (15)$$

3. LC consisting of molecules with non-uniform flexibility

3.1. Model of mesogen

For the simulation of LC consisting of rigid mesogens single particle models such as hard ellipsoids [8], hard spherocylinders [9], and the model with the Gay–Berne anisotropic potential [10] are widely used. To simulate semiflexible mesogens multiparticle models should be considered. They can be divided in two groups; ”realistic” models where the chemical structures are reproduced in sufficient details and “coarse grained” ones which take into account only the main factors necessary for the mesophase formation, such as the chain linkage of the elements, the volume interactions, and the model intrachain potentials [28]. Simulation of large systems of the first group is a very time consuming, and in practice can be used only for investigation of local processes [27]. The «coarse-grained» approximation allows simulation of the transition processes to a LC phase over a wide density range. In this work the model of the latter type is considered.

There are several simulations of LC phase using semi-flexible mesogen as a model. Allen and Wilson [4] have done MD simulations of the semiflexible LC where the mesogen was composed of seven hard tangential spheres. A hard-wall potential was used between the first and more remote neighbours in the chain. The allowed bond length fluctuations provide certain chain flexibility. Dijkstra and Frenkel [5] considered a system consisting of ten hard spherocylinders by the Monte Carlo method. Chain flexibility was introduced by a bending potential proportional to the square of the angle between adjacent spherocylinders. The density required for the LC transition in this model decreases with decreasing flexibility. Yethiraj and Fynewever [6] used Monte Carlo simulations to investigate the transition from an isotropic to a nematic state in a semiflexible LC composed of chains composed of tangent hard spherical 8 and 20 particles, with a bending potential:

$U_{bend}(\theta) = \alpha\,[1\text{-}cos\,(\theta)]$ (16)

where Θ is the valence bond angle. The flexibility of the chains was varied by changing the elastic constant α.

Kolb [7] has performed a comprehensive study of the LC state formation in the system consisting of semiflexible mesogens by using molecular dynamics simulation. His model will be used in the second and the third part of this work and will be described here in more detail.

3.1.1. Kolb's model

Kolb's mesogen model was a semi-flexible chain consisting of 6, 7 or 8 isotropic soft particles. The interactions between the particles were described by a repulsive Lennard-Jones (LJ) potential.

$$U_{LJ}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right), \quad r \le 2^{1/6}\sigma. \qquad (17)$$

Here σ and ε are *LJ's* parameters and units of length and energy correspondingly (σ =1, ε=1). Particles are bonded into the chain by a FENE (finitely extendible nonlinear elastic) potential.

$$U_{bond}(r) = U_{LJ}(r) - \frac{\varepsilon_2 R_0^2}{2\sigma^2}\ln\left(1 - \left(\frac{r}{R_0}\right)^2\right), \qquad r < R_0 \qquad (18)$$

where $R_0 = 1.5\sigma,\ \varepsilon_2 = 30\varepsilon$.

Chain flexibility was introduced by the potential given by equation (16). For such a model the persistence length l_p can be estimated as [30]

$$l_p/l=\alpha/k_BT, \qquad (19)$$

where l is the bond length. Chains of six particles were considered with values of l_p from 200 to 1000. For chains composed of 7 and 8 particles l_p was not varied (l_p=1000.) For all systems both nematic and smectic phases were observed by increase of the density. The transition density into nematic state decreased with increasing chain length or decreasing its flexibility. Along with phase behaviour the structure features of the systems were studied and dynamic properties were also considered to some extent [7].

3.1.2. Present model

In all models described above the flexibility was uniformly distributed along the chain mesogen. But in real mesogens different parts could have different flexibility, for example; the rigid central part and more flexible ends. Other types of distribution of the flexibility along the chain can be expected. In the present work we consider an example of the mesogen model with a non-uniform flexibility.

Mesogen is considered as a linear molecule consisting of N_c particles with the interaction potential (17) used by Kolb. But in contrast to his model the rigidity of a molecule is specified by introducing elastic springs between all particles (Fig.1) and the elastic energy is given by

$$U_{el} = \sum_{s=1}^{N_c-1}\sum_{i=1}^{s} U_{si} \qquad (20)$$

where the potential of the springs between i -th and s-th particles is given by

$$U_{si} = \frac{K_{si}}{2}(|r_i - r_s| - (i-s)l_0)^2 \qquad (21)$$

where l_o is the equilibrium bond length assumed $l_o = \sigma$; s is the number of neighbour particle along the chain. All springs have the same elasticity constant K_s.

In the manner of setting the flexibility our model is close to that of Allen and Wilson [4] i.e. the flexibility is specified by restrictions of distances between all particles in a chain. But in the model [4] these restrictions were introduced discretely by using hard walls; in our model elastic springs were used which allow to vary the flexibility of a mesogen by changing the elastic constant K_s .

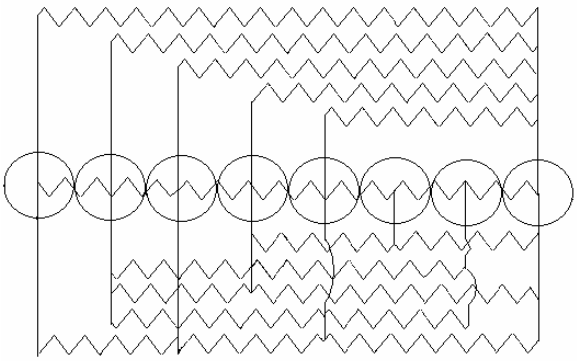

Figure 1. Layout of the model mesogen N_c=8.

3.2. Simulated systems

Two series of simulation were performed: 1) Mesogens composed of N_c =6, 7 or 8 particles with the same K_s =50; 2) Mesogens consisting of 8 particles with K_s =50, 100 and 500. The systems are referred with two numbers (table 1). The first number refers to N_c, the second – to K_s. Each system consists of $N = N_c N_m$ particles, where N_m = 1536 is the number of molecules in a simulation box.

Table 1. Parameters of simulated LC systems

System	Number of particles in chain	Persistence length of chain	Number of mesogens in the system	Type of LC phase obtained
6-50	6	59	1536	-
7-50	7	91	1536	-
8-50	8	132	1536	nematic
8-100	8	199	1536	nematic
8-500	8	430	1536	nematic

3.3. Initial structure and equilibration

The calculation was started from a regular completely ordered array of molecules on a simple cubic lattice. Molecules were aligned parallel to the long axis OZ of the simulation cell in 6 layers. The X and Y dimensions of the cell were equal to 16 to avoid the intersections of images of molecules in the neighbouring cells. The number density for this initial state is $\rho = N_m N_c / V$=1.

Equilibration of the systems was carried out using NPT ensemble. The series of calculations were conducted at progressively decreasing pressures, starting from P = 20. After the equilibration procedure the productive runs were carried out using NVT ensemble (constant temperature and volume) and various characteristics of the systems were calculated. Every productive run took $5x10^5$ steps.

3.4. Results and discussion

3.4.1. Estimation of the conformation and flexibility of the molecules

To estimate the flexibility of molecules the formula for the persistence length l_p of short chains with $L/l_p < 1$ [33] can be used:

$$< h^2 >= L^2\left[1-\frac{1}{3}\frac{L}{l_p}+\frac{1}{12}\left(\frac{L}{l_p}\right)^2\right] \qquad (22)$$

where L=(N_c –1)l_o is the contour length of the chain, l_o is the equilibrium length of the bond. The calculated values of l_p are given in the table 1. It is seen that for molecules with the same elasticity constant K_s, but with different length N_c, l_p occurs to be a function of N_c. The longest molecule is the most rigid.

For the chain with a uniform flexibility the persistence lengths can be estimated also by using the equation

$$\left\langle \cos\theta_{ij} \right\rangle = e^{\frac{-|i-j|}{l_p}} \qquad (23)$$

where Θ_{ij} is the angle between i and j bonds. For our model the nonlinear dependence of $ln <cos\ \Theta_{ij}>$ on i-j (Fig. 2) is observed. It means that the flexibility is distributed non-uniformly along the chain. The dependence of the cosine of the angle between adjacent bonds on the angle number (Fig.3) shows that molecules are more flexible at the ends and more rigid in the middle part.

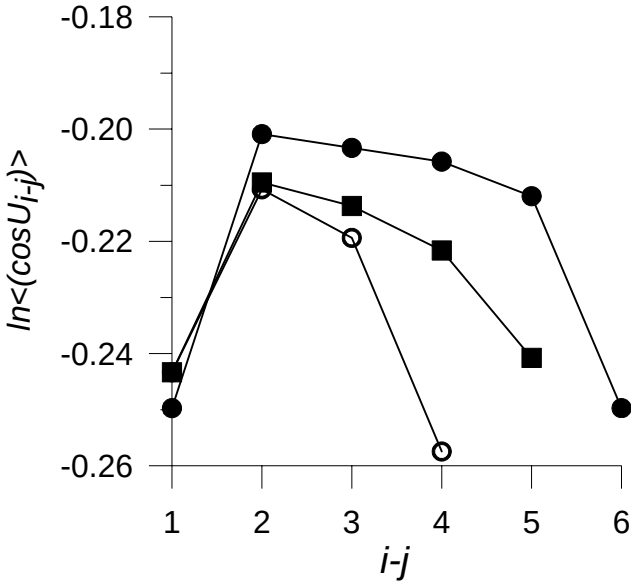

Figure 2. The dependence of *ln* <cos Θ_{ij}>. on the distance between the *i*-th and *j*-th units for a system in the isotropic state; open circles: system 6-50, squares: 7-50, filled circles: 8-50.

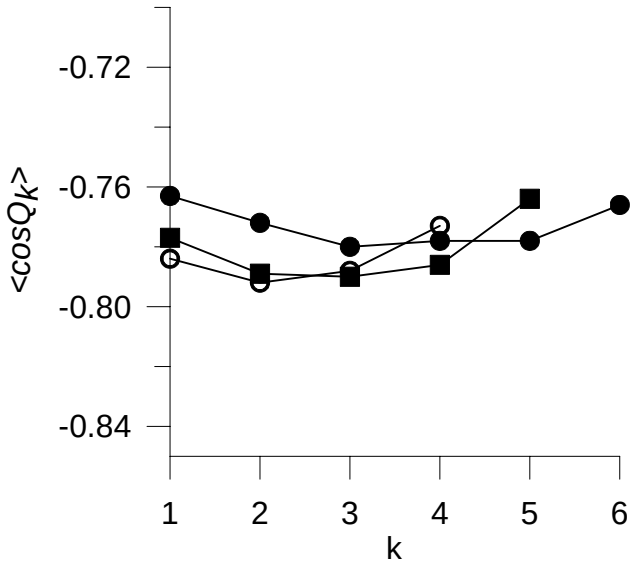

Figure 3. <cos Θ_k> dependence of the number of angle between *k* and *k +1*, segments, where segment *k* links *i* and *i+1*particles for systems considered. Open circles: system 6-50, squares: 7-50, filled circles: 8-50.

3.4.2. Order vs. density

The formation of the LC phase was followed from the behaviour of order parameter S. A fully ordered initial state of the system corresponds to S=1. With the density decrease the formation of the mesophases is indicated by a sharp decrease of the order parameter in a narrow region of density to some intermediate values S=0.6-0.9, and further decrease of density tends to formation of an isotropic phase with S close to

zero. We do not observe a mesophase formation for the systems with N_c =6 and 7.It means that these molecules are too flexible to form a LC state.

So further only the systems with N_c =8 with varying flexibility will be considered. The more flexible the molecule is the higher density is required for LC phase formation (Fig. 4). The assignment of observed mesophases to smectic or nematic LC phase was based on the calculation of structural characteristic and anisotropy of the translation mobility.

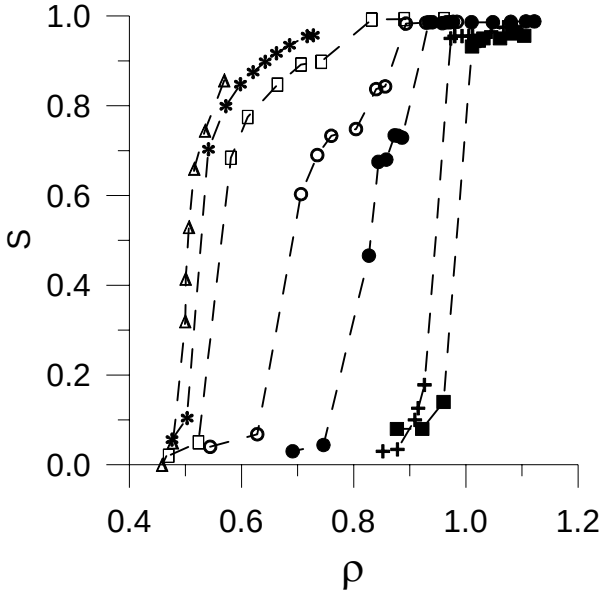

Figure 4. Order parameter dependence of density for systems considered: filled squares – 6-50, crosses -7-50, filled circles -8-50, open circles – 8-100, open squares-8-500, stars -Kolb results [7], triangles - Yethiraj and Fynewever results [6]. The lines are a guide to the eye.

3.4.3. Structure characteristic

Density distribution functions $\rho(z)$ and binary distribution functions $g(z)$ of the centres of mass of the molecules along the axis of regularity (Fig.5) show that for our systems the crystalline phase transforms directly into nematic phase. There is no indication of the layered structure characteristic for the smectic phase. The mesophase and isotropic state are characterized by a uniform density distribution along the direction of the ordering, this confirming the absence of the translational order in the system. The conclusion about the nematic nature of the LC state is confirmed by number density functions $\rho(z)$ (Fig.6).

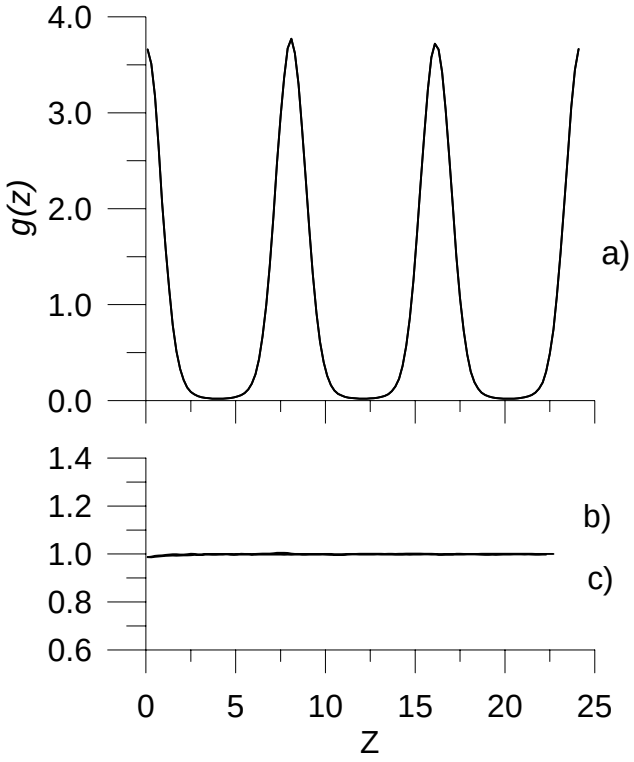

Figure 5. Binary function $g(z)$ of the distribution of molecular centres of mass along the axis 0Z for the system 8-50 a) crystalline, b) nematic, and c) isotropic phases.

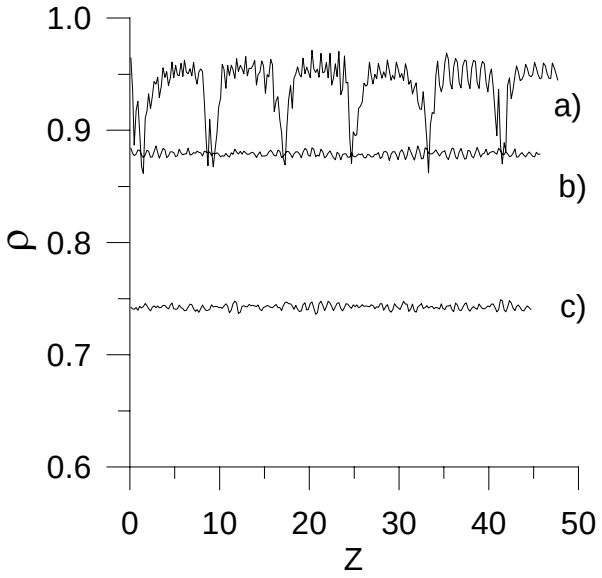

Figure 6. Density distribution functions $\rho(z)$ of mesogen monomers along the ordering axis 0Z for the system 8-50: a) crystalline, b) nematic, and c) isotropic phases.

3.4.4. Comparison with Kolb's model with a uniform flexibility

The Kolb's model is very close to our one except that the flexibility is introduced via the local potential (16). It leads to a uniform distribution of the bending flexibility

along the chain. For the persistence length l_p = 50 which is close to our value l_p = 59 the LC transition was observed even for the molecule of 6 particles. At the same time for our model LC transition was observed only for mesogen containing 8 particles. We believe that the reason for this difference is a non-uniform distribution of the flexibility along the chain in our model. Therefore not only the average flexibility but also its distribution determines the possibility of LC formation.

In addition we did not observe the formation of the smectic phase for our model. For the Kolb's model the smectic phase was not obtained only for the case N_c=6 and l_p=50. For all other considered systems both nematic and smectic phases were observed. We again connect this difference with the non-uniformity of the flexibility distribution in our model. So the flexibility distribution is an additional factor determining the nature of the LC phase along with the shape anisotropy and average flexibility of mesogens and the density of the system.

3.4.5. Comparison with theory

Usually the theory for lyotropic LC connects the jump of the order parameter ΔS and volume fractions of isotropic Φ_i and nematic phases Φ_n at the isotropic-nematic transition with ratio L / l_p. The simplest Khokhlov – Semenov theory [1] uses the second virial expansion for a hard wormlike cylinder model with the diameter d in the solution. For our case L / l_p << 1 it predicts:

$$\Delta S = 0.847 - 1.487 L / l_p \quad (24)$$

$$\Phi_i = 3.34 d / L + 4.99 d / l_p \quad (25)$$

$$\Phi_n = 4.486 d / L - 1.458 d / l_p \quad (26)$$

For the comparison with the theory we considered our molecule as a cylinder with the diameter $d = \sigma$. Figs. 7 and 8 show that our simulated values of ΔS, Φ_i and Φ_n as well as those obtained by other authors are in a satisfactory agreement with the theory predictions taking into account some uncertainty by fitting of parameters of the many particle model with soft interaction potential to those of hard wormlike cylinder and the accuracy of the theory.

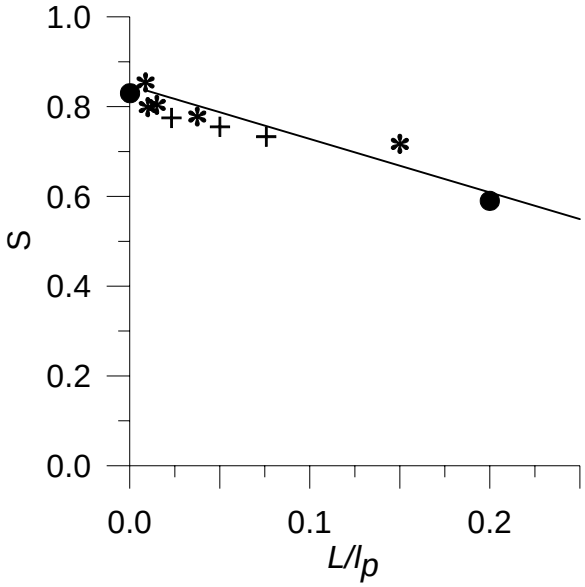

Figure 7. Jump of order parameter ΔS at isotropic-nematic transition vs. ratio of chain length L to its persistence length l_p : solid line- Khoklov-Semenov theory, crosses - our simulation results, stars-Kolb results, circles - Yethiraj and Fynewever results.

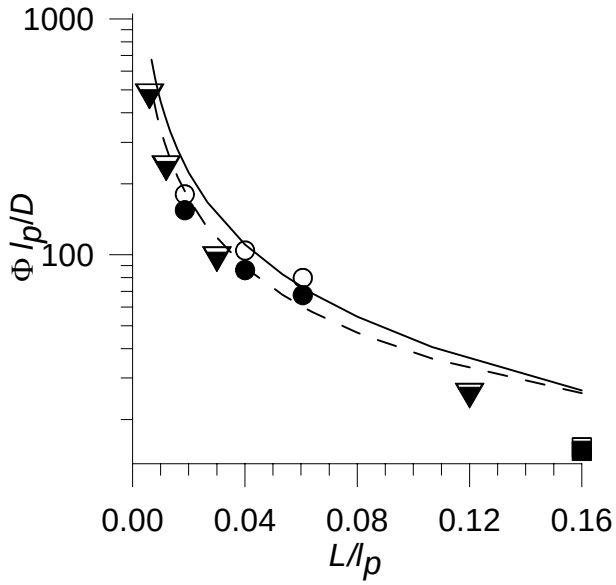

Figure 8. Scaled isotropic and nematic volume fractions at the phase transition vs. L / l_p: open symbols correspond to nematic phase, filled – to isotopic one. Circles -our simulation results, triangles - Kolb results, squares - Yethiraj and Fynewever results. Khoklov-Semenov theory results plot by lines, solid - nematic phase, dashed – isotropic phase.

3.4.6. Dynamics

3.4.6.1. Translational diffusion

The linear character of the time dependences of MSD for centres of mass of mesogens for both isotropic and nematic phase shows that the motion of mesogens has a purely diffusive character. Significantly faster diffusion along the director than in the

perpendicular direction in LC phase confirms the conclusion about the nematic nature of phase. For the diffusion coefficient along the director D_{par} a non-monotonic density dependence in the nematic phase has been observed. Similar behaviour was observed in simulations of Allen for hard ellipsoids [35] and Lowen [31] for hard spherocylinders. Such behaviour is a result of two different factors, affecting the translational motion of the mesogen in LC phase: increasing density decreases the mobility, at the same time the higher order favours the diffusion in the direction of the orientation. The flexibility also significantly affects the diffusion anisotropy in LC phase. Increase of flexibility results in lower diffusion anisotropy.

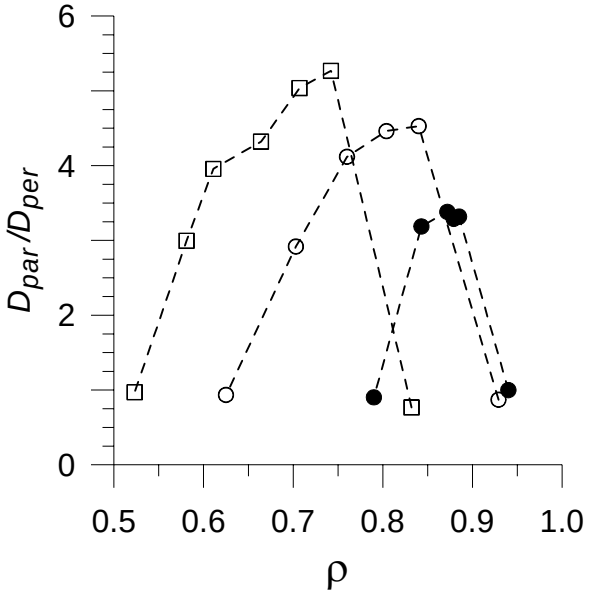

Figure 9. Diffusion anisotropy at different density for the systems with different flexibility: filled circles - l_p =132, open circles - l_p =199, squares - l_p =430. The lines are a guide to the eye.

The density dependence of the diffusion anisotropy D_{par} /D_{per} is also non-monotonic (Fig.9). The simulated values of D_{par} /D_{per} are in good agreement with experimental data and with the values obtained from other simulation models [31].

It was shown in [31] that for a concentrated solution of hard spherocylinders the anisotropy of diffusion is essentially dependent on the nematic order parameter alone. Results for our semi-flexible model reasonably fall on the same curve (Fig. 10). Therefore the conclusion about such a universal behaviour can be extended on the more broad class of nematics. The values of the anisotropy are lower than the theoretical upper limit, derived for the motion of rigid rod in a direction parallel to the orientations of the molecules [31]

$$D_{par}/D_{per} \approx \frac{2S+1}{1-S} \,. \qquad (27)$$

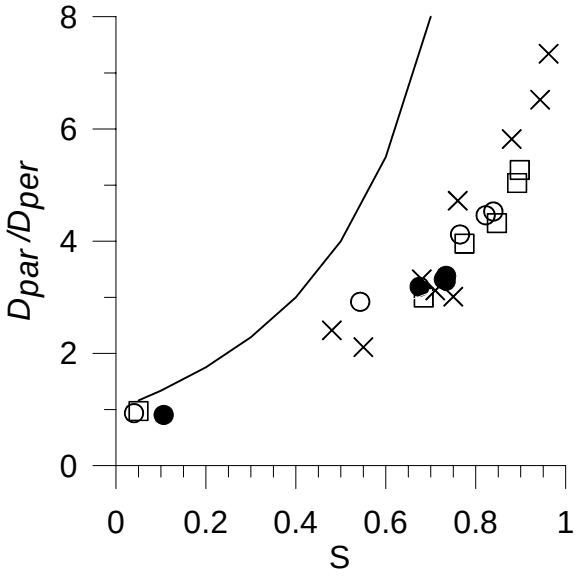

Figure 10. Diffusion anisotropy in the nematic and isotropic phase as a function of order parameter S for the systems with different flexibility. Solid line is the theoretical upper bound according eq. (27), filled circles - l_p =132, open circles - l_p =199, squares - l_p =430. The results of Lowen [31] are given by crosses.

3.4.6.2. Rotational diffusion

In the isotropic phase functions $P_1(t)$ and $P_2(t)$ decay exponentially and the relation $P_2(t) = P_1^3(t)$ is valid. It means that rotation of our mesogens can be considered as a rotational diffusion in the effective viscous medium. The calculated values D/D_{rot} for our systems is larger than the theoretical value 11.5 for rigid cylinder [32] with the same aspect ratio and increases with the flexibility of the molecule.

In the nematic state the correlation functions $P_1(t)$ and $P_2(t)$ do not decay to zero. This means that rotational motion of molecules is confined by other molecules aligned in the same direction. Rotation diffusion coefficient for this case was estimated by using the model of the wobbling in the cone (see chapter 2.1.2.2). It is interesting that the dependence of the ratio D/D_{rot} on the order parameter S (Fig. 11) for systems with various flexibilities also has an universal character. Such an universality was shown previously for hard spherocylinders [36] in the nematic phase. Thus the order parameter determines not only anisotropy of the translational diffusion but the ratio of the translational and the rotational diffusion coefficients as well for a rather broad class of nematics.

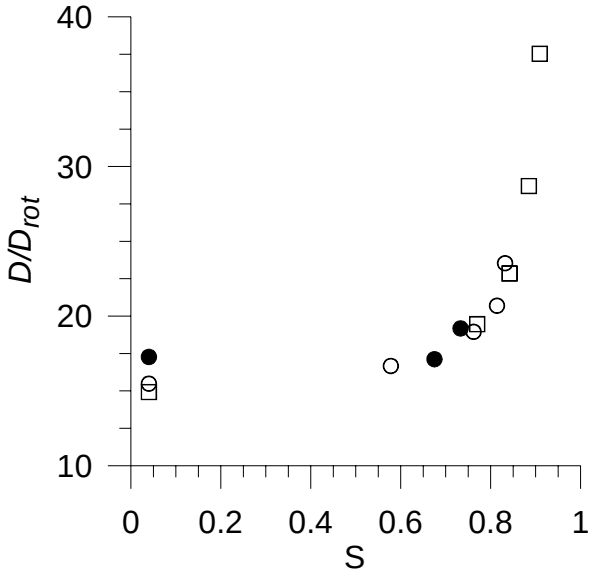

Figure 11. Ratio D/D_{rot} for isotropic and nematic phases versus order parameter S for simulated systems: filled circles - l_p =132, open circles - l_p =199, squares - l_p =430.

4. Simulation of a flexible polymer in a LC solvent

4.1. Model

As the model of the low molecular LC solvent the Kolb's model was used. This model was chosen for several reasons: 1) It was studied previously in detail, therefore its phase diagram is known; 2) It is rather simple and is close to that considered in the first section of this work; 3) It gives not only nematic but also the smectic phase at reasonable densities. The specific parameters of the model used are N_c =7 and l_p =200 [IV, V].

As a model of the polymer network a regular tetrafunctional diamond-like network consisting of flexible chains (strands) composed of 31 beads each was applied. The beads of network chains are identical to those in the network junctions and to the beads of mesogens. The chain beads are bonded by a potential (18) but without the bending potential (16).

Three composite systems with different volume fraction of LC solvent were simulated. The network containing 6 cells [IV, V] along the OZ axis and 3 cells along the OX and OY axes correspondingly was superimposed on the fully ordered initial structure of the pure LC (solvent) (chapter 3.3). The fraction of the network in the composite system is equal to 0.288. This value is close to that for real PDLC systems [37]. To study the influence of the amount of polymer on the behaviour of the composite the fraction of polymer was varied within the range 0.2-0.3 corresponding

to the real polymer dispersed liquid crystals.

Composites with larger and smaller fractions of polymer network were prepared by superimposing the same network on the regular structure of mesogens described above, but instead of six layers these systems had seven or five layers of mesogens along the OZ axis. The volume fraction of polymer in these systems was 0.328 and 0.258, correspondingly. The systems are referred to with two numbers. The first number refers to the number of the relative cells of the network, the second – to the number of layers of the mesogens. Thus, the pure LC solvent is referred to as system 0-6, the system with 6 layers of mesogens and 6 network cells as 6-6, the systems with seven or 5 layers of mesogens as 6-7 and 6-5, respectively.

In addition, the system where crosslinks were removed was considered. In this case we have a system of linear polymer chains in a low molecular LC solvent. The fraction of polymer was 0.285, which is almost the same as in the system 6- 6. The system is referred to as 6*-6 system.

4.2. Equilibration

After the preparation of the initial structure, its conversion and equilibration were started followed by production run. The special procedure of the equilibration was elaborated taking into account the large overlapping of particles in the initial structure. The process of the equilibration is described in publication [IV].

4.3. Results and discussion

4.3.1. Network influence on order parameter

For all systems the sharp increase of the order parameter in the narrow region of the density is observed indicating the formation of the LC phase. The main effect of the polymer addition is the shift of the curve $S(\rho)$ to higher densities (Fig.12). There is no remarkable difference between curves corresponding to different volume fractions of the LC solvent, which changes in the range from 0.67 to 0.74. Removing of junctions does not lead to a visible change of dependence $S(\rho)$.

The same LC solvent phases (nematic and smectic) as for the pure LC are observed for the composite systems. Snapshots [IV] demonstrate some microphase separation between polymer and mesogens. The separation is minimal in the isotropic phase and increases at the transitions to nematic state and further from nematic to smectic state.

The attribution of the phase state as a nematic or smectic phases was performed using structural data, snapshots and the analysis of diffusion anisotropy of mesogens.

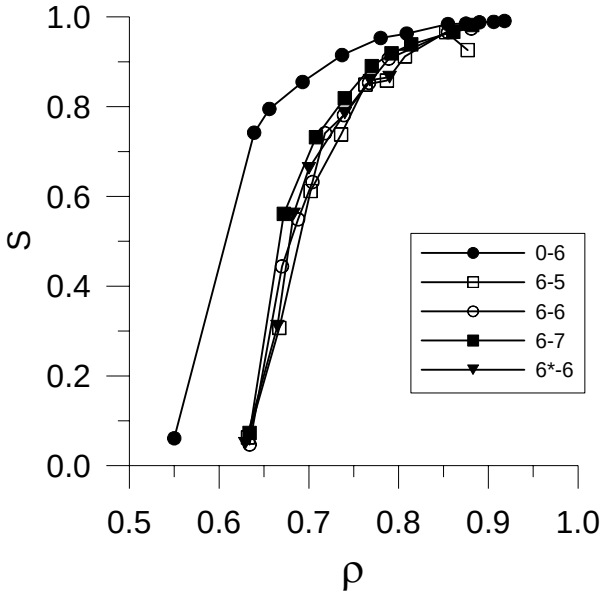

Figure12. Dependence of the order parameter of the LC solvent on the density for the systems considered. The lines are a guide to the eye.

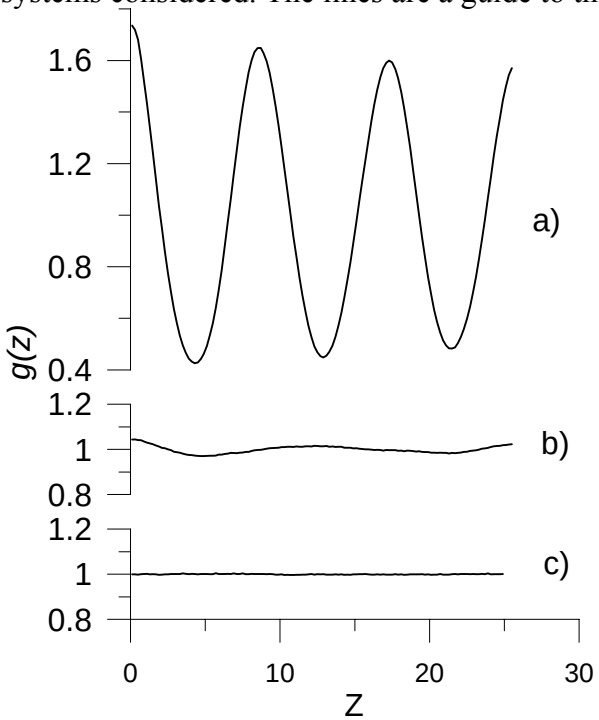

Figure 13. Binary distribution function *g (z)* of the centres of mass of mesogens along OZ axis for the system 6-6: a) smectic, b) nematic and c) isotropic phase.

4.3.2. Structural characteristics

4.3.2.1. LC and network layering

Fig. 13 shows the binary distribution functions g(z) for centres of mass of mesogens along the axis of the regularity OZ.

The distribution is uniform for nematic and isotropic phases. For the smectic phase the periodic character corresponds to the layered structure of the LC solvent. In simulated systems the number of layers was equal to that in the initial state.

The morphology of the composite was characterized by the density profiles of beads belonging to mesogens and to the polymer chains along OZ (Fig. 14).

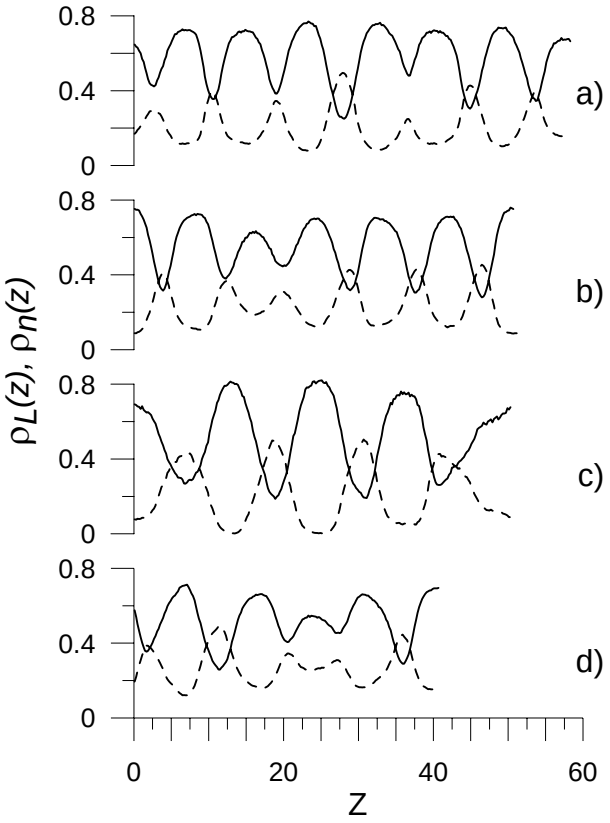

Figure 14. Number density distribution of LC beads (solid line) and network beads (dashed line) along OZ axis for smectic phase: a) 6-7 b) 6-6, c) 6*-6 d) 6-5 system.

In the smectic phase mesogen and network beads are distributed periodically and the maximum of $\rho_L(z)$ corresponds to the minimum *of* $\rho_n(z)$ and vice versa. In the nematic phase small peaks remain reflecting the microphase separation between LC and network beads but their positions loose the periodic character. In an isotropic state LC and network beads are distributed practically uniformly [IV].

Fig. 14 shows density distributions in the smectic phase for systems with the same number of network cells but with different number of LC layers. The beads of network are distributed mainly between the smectic layers of mesogens and the number of layers occurs to be always equal to the number of layers of LC solvent along the OZ axis. Therefore the transition of the LC solvent into the smectic state disturbs the network morphology and the periodicity of LC phase determines the

number of network layers. It means that some chains belonging initially to different cells combine in the same interlayer if the number of network layers exceeds that of the solvent. In the opposite case chains belonging to the same cell redistribute over neighbouring unterlayer regions. For nematic and isotropic states there is no any significant difference between network density distribution for different systems. The junctions of polymer network are also redistributed between the layers of LC in the smectic phase. In nematic and isotropic state their distribution is practically uniform [IV].

4.3.2.2. Linear polymer chains in LC solvent

This system was prepared in the similar way as the system 6-6 but without crosslinks between chains. The transition into nematic state occurs in the same density region. However the transition into smectic phase occurs at smaller density than for the system with the network, i.e. the network hinders the formation of the smectic phase as compared with linear chains. The morphology in the smectic state has also changed. Initial six LC layers transformed into five layers. Correspondingly, polymer beads redistribute into five interlayer regions. Such morphology corresponds to a more profitable space packing at a given density than the initial six layer structure [IV].

4.3.2.2.1 Conformations of polymer chains in LC solvent

The distribution functions of the end-to-end distance of the network chains g($h\rho^{1/3}$) in the different LC states of the solvent for the system 6-6 are shown in Fig. 15. In the isotropic state the distribution is narrow and symmetric. In the nematic state there is a weak broadening in the region of larger distances due to the alignment of network chains along the nematic director.

In the smectic phase there is a shoulder from the side of larger h. At the same time the maximum of the distribution is shifted to smaller h reflecting the accumulation of the network chains in the interlayer space. The network chains connecting junction located in different interlayers become stretched, while the chains within the same interlayer space shrink in the direction of the axis of regularity. This conclusion was confirmed by calculating the projection of the mean-squared end-to-end distance of the chains [IV].

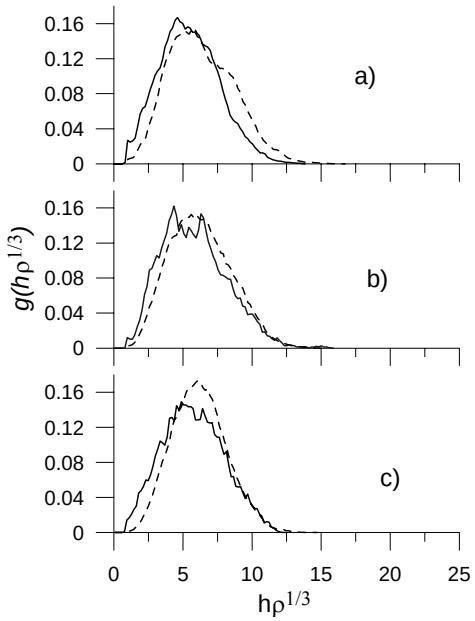

Figure 15. End-to-end distance distribution of linear polymer chains (system 6*-6) (solid line) and network strands (system 6-6) (dashed line) in LC solvent at different LC phases of solvent: a) smectic, b) nematic, c) isotropic phase.

In the system LC with linear chains (6*-6) some changes of chain conformations are observed. Both in the isotropic and nematic phases the function $g(h\rho^{1/3})$ is broader than for network chains (system 6-6) (Fig.15b,c). This difference reflects the possibility of larger fluctuations of chain end-to-end distances in the non-crosslinked system.

In the smectic phase free chains can accumulate in interlayers and no shoulder on the $g(h\rho^{1/3})$ is seen (Fig.15a). The maximum $g(h\rho^{1/3})$ is shifted to smaller h, compare to the nematic phase due to the shrinkage in the Z direction of chains accumulated in the interlayers. This behaviour is in good agreement with the results obtained by Kolb [7] for a single flexible chain in a LC solvent.

4.3.3. Dynamics

4.3.3.1. Translational mobility of mesogens in the composite system

In the pure LC solvent the translational motion of mesogen is also diffusive as in the model considered in the section 3.4.6.1. In LC state there is an anisotropy of diffusion: $D_{par} / D_{per} > 1$ for the nematic phase and $D_{par} / D_{per} < 1$ for the smectic phase. Thus, in the composite systems the translational mobility of a mesogen has the same character as in pure LC. In the nematic phase the diffusion coefficient D_{par} is

non-monotonic vs. density both in pure LC solvent and in the composite systems. Qualitatively the anisotropy of diffusion changes similarly both for pure LC solvent and for composite systems with the density of the system, however the maximum value of D_{par} / D_{per} for composite systems is less than that for the pure solvent, due to the smaller value of D_{par} (Fig. 16).

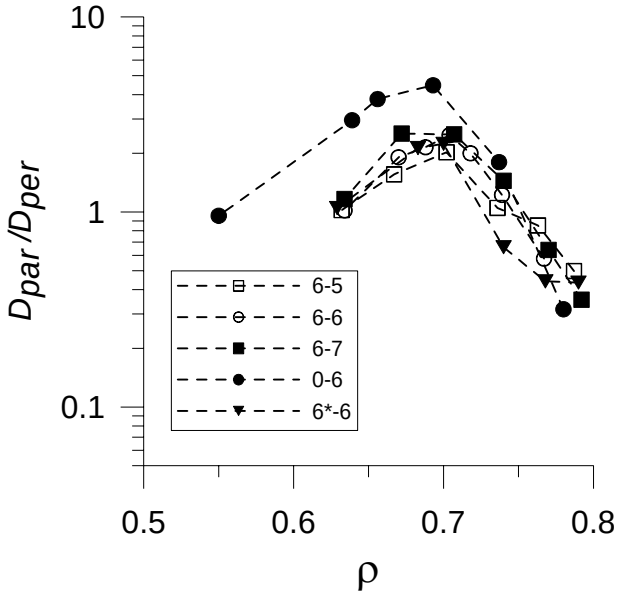

Figure 16. Diffusion anisotropy at different densities for the composite systems. The lines are guides to the eye.

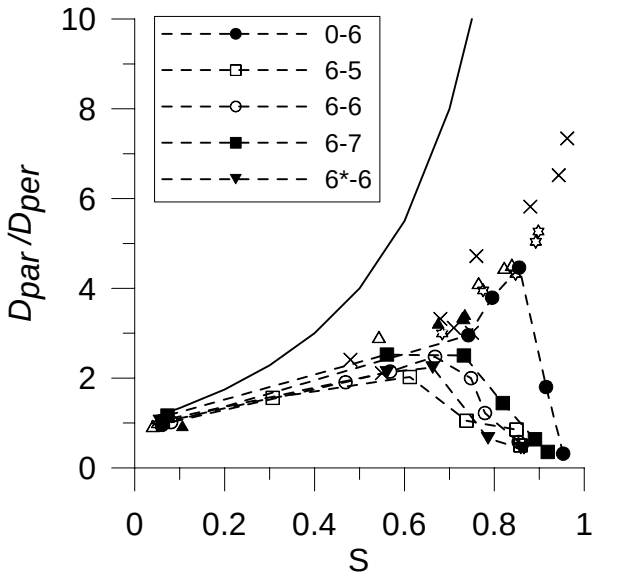

Figure 17. Diffusion anisotropy as a function of order parameter S for LC. Solid line is the theoretical upper bound according eq. (27); downward triangles, open triangles and six point stars are the data for mesogens with the non-uniform flexibility [III], crosses - the results of Lowen [31].

The conclusion about the universal character of the dependence of the diffusion

anisotropy on S in nematic phase appears to be valid in the presence of a polymer also. All the points fall reasonably near a single curve (Fig. 17). The deviation of anisotropy of diffusion from of the single curve at larger S is related to the transition from the nematic to the smectic state.

4.3.3.2. Rotational mobility of mesogens in the composite system

To estimate the rotational mobility of mesogen in the composite system the same procedure as described in chapters 2.1.2.2 and 3.4.6.2 was used.

In an isotropic state the value D/D_{rot} is larger than the theoretical value 9 for a rigid rod but is practically the same for all composite systems (13.3-15.3). This result and the approximate validity of the relation (11) allows to conclude that the rotation of a mesogen even in the presence of polymer can be considered as a rotational diffusion in a viscous medium. For the description of the rotation of a mesogen in the nematic and smectic phases the model of wobbling in a cone was applied as for pure LC [III].

In the nematic phase values of D/D_{rot} for the composite systems are larger than those for pure LC solvent at the same S (Fig. 18). Polymer restricts the rotational mobility of a mesogen to a larger extent than the translational one. The effect of the network is stronger than that of linear chains at the same S.

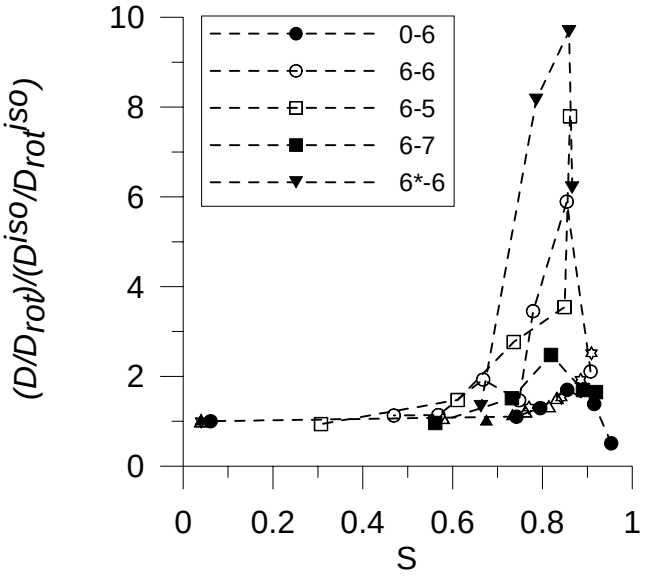

Figure18. The ratio D/D_{rot} reduced to the values of this ratio for the corresponding isotropic state vs. order parameter S for all the systems considered. Downward triangles, open triangles and six point stars are the data for mesogens of various flexibility [III].

In the nematic-smectic transition region the systems behave in a different way. In

pure LC solvent the ratio D/D_{rot} slightly decreases with increase of S. In contrast to the composite system there is a sharp peak for this ratio. The highest peak is for the system with linear polymer chains. For systems with network this height decreases with the decrease of the fraction of network. Analysis shows [V] that D_{rot} significantly decreases in the transition region. After the formation of true smectic phase the ratio decreases.

Thus the polymer in the composite system mainly restricts the rotational mobility of mesogens and this effect is more pronounced in the nematic-smectic transition region.

4.3.3.3. Local mobility of the network

The translational mobility of the network was studied by calculation of MSD for network junctions and middle chain monomers separately.

Time dependences of MSD for monomers are linear in a log-log scale. The slope decreases with transition from the isotropic to the smectic phases. Analysis shows that this decrease reflects the enhancement of restrictions imposed on the chain motion by the ordering of the LC solvent. Maximum restrictions are observed, as expected, in the smectic phase where chains are located in interlayer regions.

To study the effect of the shape of LC solvent molecules on the mobility of network chain monomers the system of network in isotropic solvent was simulated additionally where long mesogens were substituted by short dumbbells keeping constant the volume fraction of the solvent. The mobility of monomers in this system was higher but the slope of the MSD time dependence in log-log scale was the same. It means that the solvent consisting of long mesogens can be considered as a viscous medium for chain monomers.

LC ordering of the solvent results in some anisotropy of translational mobility of chain monomers: the diffusion of network beads along the axis of order is faster than in the perpendicular direction in the nematic phase and vice versa in the smectic phase (Fig. 19).

The MSD of crosslinks show approximately the same slopes as the MSD of chain monomers for corresponding LC phase of the solvent. The ratio of the MSD of middle chain monomers to that of crosslinks is about 1.7, slightly less than the theoretical value 2 for the network of Rouse chains [38, 39].

In the nematic state anisotropy of diffusion of crosslinks is less than for chain

monomers. In the smectic phase degree of the anisotropy of crosslinks and chain particles is practically the same.

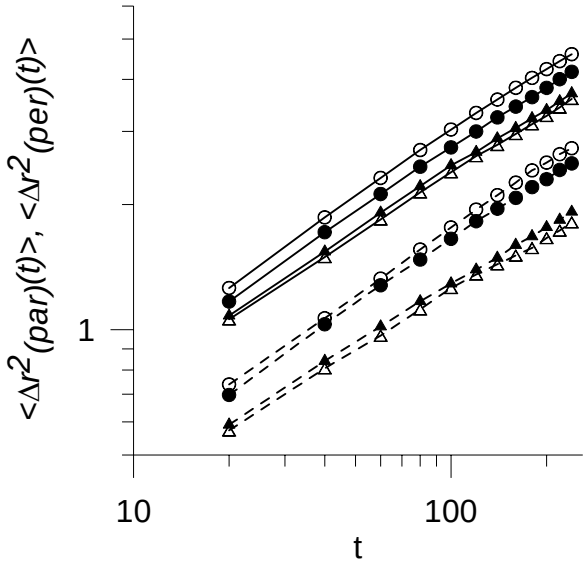

Figure 19. Time dependences of MSD of middle chain monomers (solid lines) and crosslinks (dashed lines) for the system 6-6: triangles – smectic (ρ=0.789), circles – nematic (ρ=0.704). Open symbols - $< \Delta r^2_{par}(t) >$, filled symbols - $< \Delta r^2_{per}(t) >$.

4.3.3.4. Translational mobility of linear polymer chains

When the cross-links were deleted the mobility of chain monomers increased.

The values of MSD and the slopes of corresponding time dependences (in log-log scale) are larger than for the cross-linked systems discussed above.

The anisotropy of diffusion of monomers of the linear chains has the same sign as that of a polymer network in the corresponding mesophase of LC solvent. However the degree of the anisotropy for linear chains is more pronounced, especially for the smectic phase. It can be due to the averaging of MSD calculations for the network systems over all the network strands: both parallel and perpendicular to the director. In the smectic phase linear chains concentrate in interlayer regions and the number of interlayers is less than in the cross-linked system.

5. Simulation of LC elastomers

5.1. Model of LC elastomer

For the preparation of the polymer network with side chain mesogens (LC elastomer) a special procedure was elaborated. As an initial one the systems 6-6 of polymer network in low molecular LC solvent considered above was used. In the system

obtained after sufficiently long trajectory the reaction of the attachment of ends of mesogens to the network was simulated. When one of the mesogen ends was in the close vicinity of a free chain monomer a new FENE bond was introduced between them. Bond formation was carried out using the NVT ensemble until the degree of conversion equal to 99% was achieved [VI]. After that the system was equilibrated as described in chapter 2.1.

5.2. Structural features

The dependence of the order parameter of mesogens on the total density of the system with attached mesogens (LC elastomer) and the system 6-6 of network in LC solvent is shown in Fig. 20. The attachment of mesogens to the network results in a decrease of the order parameter S at the same density. The assignment of obtained LC phases was carried out as in the previously described systems: on the base of structural and dynamical data. For the LC elastomer all three phases were observed: isotropic, nematic and smectic ones. Nematic phase forms in the same density region as in the initial composite system. The main difference is observed for the smectic phase: it appears at lower densities than in the composite system, i.e. the density range of the existence of the nematic phase is narrower and that of the smectic phase is broader than for the corresponding composite [VI].

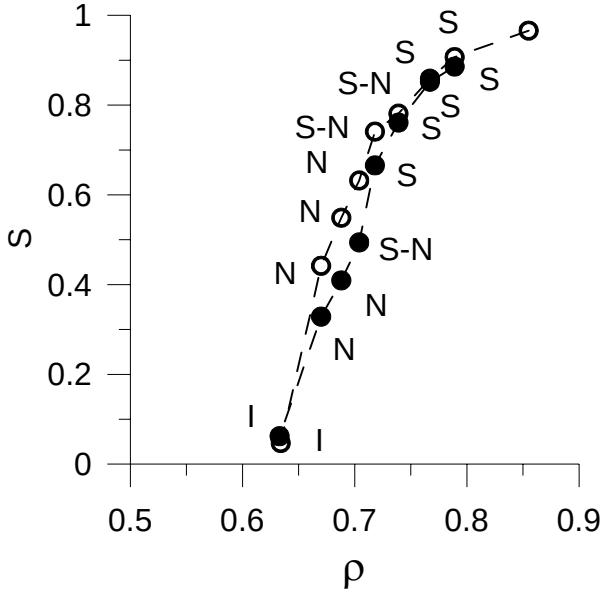

Figure 20. Order parameter vs. density: here: I – isotrop, N-nematic, S- smectic phase. Open circles: network in LC solvent, filled circles - LC elastomer.

In the LC elastomer the periodic structure in the smectic phase is more pronounced

than in the composite network/LC system at the corresponding density. In the smectic state the end-to-end distance distribution *g (h)* of network polymer chains in LC elastomer is shifted to higher *h*. It means that main chains with mesogenic side groups in the smectic state are stretched in comparison to those in the smectic LC solvent.

5.3. Translational mobility in LC elastomers

Transformation of the composite system into LC elastomer leads to the decrease of the translational mobility of both the mesogen and the main chain monomers [VI]. Due to the attachment of the mesogen to the main chain the time dependence of MSD for the mesogen becomes non-linear. Also the attachment of mesogens to the network results in the decrease of the slope of time dependences of MSD (in log-log scale) of the middle chain monomers of the network (Fig.21).

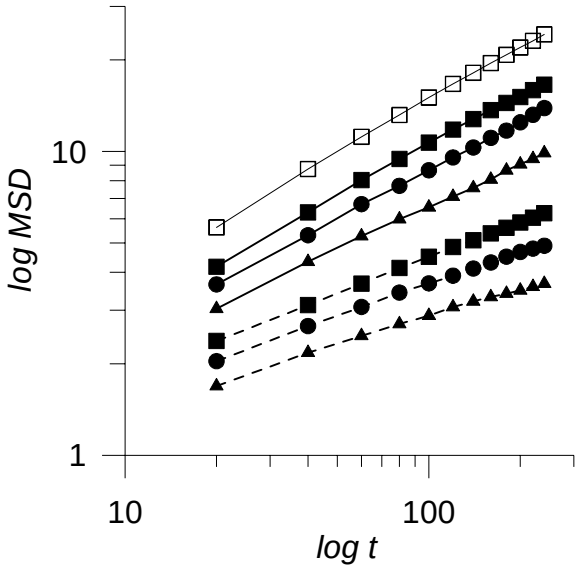

Figure 21. Time dependences of MSD of middle chain monomers of network in composite network/LC system (solid lines) and LC elastomer (dashed lines) system: triangles – smectic (ρ=0.789), circles – nematic (ρ=0.704), squares- isotropic phase ((ρ=0.634). Open squares- network in monomer solvent.

The anisotropy of diffusion (Fig.22) has the same character as in the system with non-attached mesogens. To estimate the value of anisotropy the ratio $< \Delta r^2_{(per)} > / < \Delta r^2{}_{(par)} >$ vs. time was used. For the system with attached mesogens this ratio is higher for the smectic phase and lower for the nematic phase than in the composite system. Thus the anisotropy of translational diffusion is less pronounced in LC elastomer than in network/LC system.

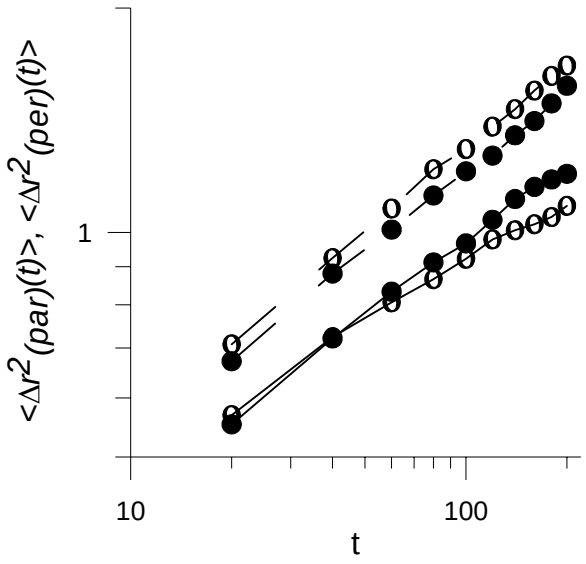

Figure 22. Time dependences of MSD of mesogen in smectic (solid lines) and in nematic phase (dashed lines) of LC elastomer. Open symbols - $< \Delta r^2_{(par)}(t) >$, filled symbols - $< \Delta r^2_{(per)}(t) >$.

To estimate the anisotropy of diffusion of the network polymer chains the same procedure as for polymer network in low molecular LC solvent was used (chapter 4.3.3.3). The anisotropy of translational mobility of the network chains reflects higher structural anisotropy of LC elastomer system and it is more pronounced in the smectic phase [VI].

6. Conclusions

Molecular dynamics simulation was used to study the structural and dynamical properties of a LC complex system. Three systems which are able to form lyotropic LC state were considered. The first is the system of short semiflexible linear molecules (mesogens) with non-uniform distribution of flexibility along the chain. The second is a flexible polymer network swollen in solvent consisting of mesogens with uniform flexibility. The third one – a polymer network consisting of crosslinked polymer chains with mesogenic side groups.

1. It was shown that the non-uniform flexibility results in the absence of the smectic phase in the density region where mesogens with uniformly distributed flexibility form such a phase. At the same time the simulated characteristics of the isotropic – nematic transition agree rather well with the theory predictions and with the results of simulations for semi-flexible mesogens with a uniform flexibility.

The dependences of anisotropy of the translational diffusion and the ratio of translational to the rotational diffusion coefficient on the order parameter coincide with those for rigid mesogens and mesogens with uniform flexibility, suggesting a universal behaviour.

2. The composite system of a polymer in LC solvent forms the same phases by an increase of the density: isotropic, nematic and smectic phase as in the case of a pure solvent. The presence of network shifts the isotropic-nematic transition to higher densities compared to the pure LC solvent. The position of the smectic-nematic transition is not affected by the presence of a polymer. The effect of the structure of the LC solvent in the smectic phase on the morphology of network was revealed. In addition, the stretching of network strands along the direction of order and its shrinkage in the perpendicular direction was observed. This effect is more pronounced in the smectic phase.

For the system consisting of non-crosslinked chains swollen in the LC solvent the transition into the smectic phase leads to concentration of chain monomers in the interlayer regions.

The presence of flexible polymer decreases the diffusion of mesogens along the axis of regularity and results in lower anisotropy of the translational diffusion. However, the universal dependence of the diffusion anisotropy on the order parameter in the nematic phase remains also in the presence of polymer.

The sign of the anisotropy of the translational mobility of chain monomers and crosslinks corresponds to that of the mesogens.

It was shown that the network restricts the rotational mobility of mesogens to a larger degree than the translational mobility.

3. The special procedure was elaborated for the formation of the LC elastomer with side chain mesogens. The structural and dynamical behaviour of side chain LC elastomer was studied and compared with corresponding systems of polymer network in low molecular LC solvent. In LC elastomer the region of the existence of the nematic phase is narrower and that of the smectic phase is broader than in the corresponding composite system.

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